Sum rules for the squared modulus of the nonlinear Raman susceptibility

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We construct new sum rules for the nonlinear susceptibility modulus of Raman processes using the complex analysis proposed in a previous paper [K.-E. Peiponen, Phys. Rev. B 37, 6463 (1988)]. The validity of the sum rules is confirmed by the Lorentzian line-shape approximation for the Raman susceptibility.

I. INTRODUCTION

From classical dispersion theory, we know that various angular-frequency-dependent linear optical constants are related via the Kramers-Kronig relations;[1] e.g., the refractive index is related to the extinction coefficient. To obtain more information about the optical constants as a function of angular frequency, one gives sum rules that characterize the optical properties of the medium. So far many investigators have given sum rules using, e.g., powers of the optical constants, different weighting functions, and different types of their derivations.[2–11] Recently, in addition to the case of linear susceptibilities, the Kramers-Kronig-type dispersion relations and sum rules were also introduced for nonlinear susceptibilities.[10–14] The derivations given in Refs. 11–14 were based on the use of the results of the theory of several complex variables.

In this paper we derive a sum rule to describe the nonlinear Raman susceptibilities, and we give a discussion on whether it is possible to give sum rules for the squared modulus of the nonlinear susceptibility. For its confirmation, we investigate the intensity data of coherent anti-Stokes Raman spectra (CARS).

II. DISPERSION RELATIONS AND SUM RULES

One of the present authors described the nonlinear susceptibility as a function of several complex angular-frequency variables.[14] In Ref. 14, the original physical complex frequency planes (called physical planes hereafter; the real axes of these planes have a physical meaning, actually) were transformed into unit disks using a conformal mapping, and then the nonlinear susceptibility as a holomorphic function was expanded to a power series in a polydisk.

When we obtain the coherent Raman spectrum of either CARS or Raman-induced Kerr-effect spectra (RIKES), we use a pumping light with a constant wavelength (the corresponding frequency is defined as ω_2) and a probe light whose wavelength (ω_1) is scanned. This means that in these four-wave-mixing processes we essentially have two independent angular frequencies: one is fixed, the other is variable. Therefore the total susceptibility, which is the sum of the nonresonance background term $\chi_{\rm NR}^{(3)}$ and Raman term $\chi_R^{(3)}$, is given, in a polydisk, by the following series expansion of two variables z_1 and z_2:

$$\chi^{(3)}(z_1,z_2)=\sum_j \sum_k a_{jk} z_1^j z_2^k \ , \tag{1}$$

where $z_n=(\hat{\omega}_n-i)/(\hat{\omega}_n+i)$, $n=1,2$. This series can be considered as a series expansion $\sum_l c_l(z_2)z_1^l$ of one variable z_1 only, with complex coefficients $c_l(z_2)$. The function of Eq. (1) is an analytic function of the variable z_1.

One may ask: "Do the dispersion relations exist in the unit disk like in the physical plane?" The answer is "yes." We can give dispersion relations using the Poisson theory for a disk, as presented in a book by Morse and Feshbach[15] as follows:

$$(\chi^{(3)}(e^{i\theta_1'},e^{i\theta_2}))^r=(\chi^{(3)}(0,e^{i\theta_2}))^r-\frac{i}{2\pi}\mathrm{P}\int_0^{2\pi}(\chi^{(3)}(e^{i\theta_1},e^{i\theta_2}))^r\cot\left[\frac{\theta_1-\theta_1'}{2}\right]d\theta_1 \ , \tag{2}$$

where θ_2 is constant, $r=1,2,\ldots$, P denotes the Cauchy principal value, and $z_1=\exp(i\theta_1)$ and $z_2=\exp(i\theta_2)$.

The function of the left-hand side of Eq. (2) is analytic. The validity of Eq. (2) is shown by, e.g., Moretti[16] for an arbitrary analytic function. Sum rules are obtained if we simply choose $\theta_1'=2\pi$ which corresponds to the frequency value $\omega_1=\infty$ in our original physical plane. This leads to $\chi^{(3)}(1,\theta_2)=0$. If we return to the physical plane, we

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have

$$\int_{-\infty}^{\infty} \frac{\mathrm{Im}[\chi^{(3)}(\omega_1,\omega_2)]\omega_1}{\omega_1^2+1} d\omega_1 = -\chi^{(3)}(0,\omega_2)\pi ,$$
$$\int_{-\infty}^{\infty} \frac{\mathrm{Re}[\chi^{(3)}(\omega_1,\omega_2)]\omega_1}{\omega_1^2+1} d\omega_1 = 0 \quad (3)$$

in the case $r=1$. Here we used $d\theta_1=2d\omega_1/(\omega_1^2+1)$ and $\omega_1=-\cot(\theta_1/2)$. The first sum rule in Eq. (3) has the same form as the sum rule which was given by King[5] for the linear refractive index. Taking into account that the integrals appearing in Eq. (3) exist as normal integrals, it is not necessary to calculate the Cauchy principal value. The dispersion relation of Eq. (2) and the sum rule of Eq. (3) are generalized to hold for a nonlinear susceptibility of several angular-frequency variables by using the same method, which is shown in Refs. 12 and 14. We, however, do not write these formulas explicitly here, because the derivation is quite evident and our purpose is mainly to study the squared modulus of the nonlinear susceptibility.

The squared modulus can be approximated as follows:

$$|\chi^{(3)}(z_1,z_2)|^2 \simeq \left[\sum_{l=0}^{N} c_l(z_2) z_1^l\right]\left[\sum_{l=0}^{N} \bar{c}_l(z_2)\bar{z}_1^l\right] . \quad (4)$$

Using the Cauchy formula and taking into account $z_1\bar{z}_1=1$, we obtain a new sum rule

$$\frac{1}{2\pi i}\int_{|z_1|=1} \frac{|\chi^{(3)}(z_1,z_2)|^2}{z_1} dz_1 = \sum_{l=0}^{N} |c_l(z_2)|^2 \quad (5)$$

in the unit disk. In the case of the series expansion of Eq. (1), the right-hand side of Eq. (5) is modified to be the sum of the two series

$$\sum_j a_{jj}^2 + 4a_{00}\sum_{k\neq 0} a_{0k}\mathrm{Re}(z_2^k) .$$

The latter part of the two series is dependent on the wavelength of the pumping laser. If the wavelength of the pumping laser is scanned, the similar integrations with respect to both variables z_1 and z_2 using Eq. (5) yield only the series $\sum_j a_{jj}^2$. In Ref. 14, it was proposed that the real and imaginary parts of the nonlinear susceptibility can be calculated using the squared modulus of the susceptibility. In such a calculation, the series expansion of Eq. (1) is truncated. The sum rule of Eq. (5), together with Eq. (1), allows us to estimate the index value for which the series can be truncated. In the physical plane, Eq. (5) yields

$$\int_{-\infty}^{\infty} \frac{|\chi^{(3)}(\omega_1,\omega_2)|^2}{\omega_1^2+1} d\omega_1 = \pi\sum_{l=0}^{N} |c_l|^2 . \quad (6)$$

Let us first examine the validity of the formula of Eq. (6) by using a single Raman-mode model[17–19] which is frequently used to describe the nonlinear Raman susceptibilities, i.e.,

$$\chi^{(3)} = \chi_{\mathrm{NR}}^{(3)} + \chi_R^{(3)} = \chi_{\mathrm{NR}}^{(3)} + \frac{R}{\omega_R-(\omega_1-\omega_2)+i\Gamma} . \quad (7)$$

If we substitute $\delta=[\omega_R-(\omega_1-\omega_2)]/\Gamma$, $z=(\delta-i)/(\delta+i)$, we have

$$\chi^{(3)} = \chi_{\mathrm{NR}}^{(3)} - \frac{iR}{2\Gamma}(1-z) . \quad (8)$$

Thus we have only two terms in our series expansion with the coefficients $\chi_{\mathrm{NR}}^{(3)}-iR/2\Gamma$ and $iR/2\Gamma$. A straightforward integration of the left-hand side of Eq. (6) with respect to the present variable δ gives the sum of the squared moduli of these coefficients. This indicates that our model is reasonable.

Recently we calculated the effective Raman susceptibility for benzene[20] using the experimental data given by Levenson.[21] In the present work, we have confirmed that the result of Ref. 20 is consistent with the sum rule of Eq. (5). Therefore it is concluded that the sum rules of Eqs. (5) and (6) can be used to check whether the calculated real and imaginary parts of the susceptibility are reasonable or not.

Next we present another useful sum rule. A generalized dispersion relation was given in Ref. 14, but it has not been fully understood until now. This relation seems to be a key to the formulation of new types of sum rules for the intensity quantities in the physical plane. We give the following relation known as the generalized Cauchy formula:[14,22]

$$|\chi^{(3)}(z_1',z_2)|^2 = \frac{1}{\pi i}\mathrm{P}\int_{|z_1|=1} \frac{|\chi^{(3)}(z_1,z_2)|^2}{z_1-z_1'} dz_1 - \frac{1}{\pi}\int\int_{|z_1|\leq 1} \frac{\frac{d}{d\bar{z}}[|\chi^{(3)}(z_1,z_2)|^2]}{z_1-z_1'} d(\mathrm{Re}z_1)d(\mathrm{Im}z_1) , \quad (9)$$

where the derivative $d/d\bar{z}$ is defined as

$$\frac{d}{d\bar{z}} = \frac{1}{2}[d/d(\mathrm{Re}z_1)+id/d(\mathrm{Im}z_1)] .$$

In the Appendix we describe briefly how to calculate the surface integral of Eq. (9) in the case that the nonlinear susceptibility is expressed by a series expansion such as Eq. (1) with a constant z_2.

We tried to convert the result of Eq. (9) to our physical plane. In such a procedure we meet difficulties. The surface integral of Eq. (9), involving the complex derivative, must be integrated in the whole upper half plane. However, it is the real axis that corresponds to the measurable physical quantity, i.e., angular frequency. It seems that we can calculate the surface integral only for the case that we can form the complex derivative, e.g., for the

Lorentzian line-shape model. For the Lorentzian or more complicated model, the sum rule of Eq. (9) can be transformed into the physical plane after forming the Jacobian determinant[23] needed for the conversion, although we have not done it explicitly.

Using Eq. (8), we can write the squared modulus as follows:

$$|\chi^{(3)}|^2=(\chi^{(3)}_{\mathrm{NR}})^2+\frac{\chi^{(3)}_{\mathrm{NR}}}{2\Gamma}(z-\bar{z})+\frac{1}{4}\frac{R^2}{\Gamma^2}(1-z-\bar{z}+z\bar{z})\,, \tag{10}$$

from which it is possible to calculate the surface integral in the unit disk. The value of the contour integral is $(\chi^{(3)}_{\mathrm{NR}})^2+\frac{1}{2}(R^2/\Gamma^2)$ for the case of $z=-1$, i.e., for the Raman resonance, whereas the value of the surface integral is $\frac{1}{2}(R^2/\Gamma^2)$. Thus these two integrals give equal value to the Raman susceptibility.

When we convert the contour integral to the physical plane, we have to preserve the Cauchy principal value. In this conversion, the contour integral is decomposed into real and imaginary parts. The real part of the integral has the same form as the integral of Eq. (6) for the $z=-1$ case, whereas the imaginary part vanishes as a principal value for a case where the squared modulus of the susceptibility is an even function of the variable. These calculations are straightforward and completed by substituting $z=(\delta-i)/(\delta+i)$ into the contour integral of Eq. (9). If the imaginary part of the contour integral would not vanish as a principal value, it is canceled by the surface integral. The cancellation is made because the left-hand side of Eq. (9) must have a real value.

Using the sum rule of Eq. (9), we have also made various numerical integrations by changing the curve parameters for the case where the Raman susceptibility has the form $R[\omega_R^2-(\omega_1-\omega_2)^2+i\Gamma]^{-1}$. The result of the calculation shows that the contribution of the surface integral can be considerably large and not negligible.

III. SUMMARY

As a summary, in this paper, we have considered the squared modulus of Raman susceptibilities using the theory of complex analysis and constructed sum rules. It was difficult, in the physical plane, to interpret the result of the sum rule obtained using the general dispersion relation, since the surface integral contains a complex derivative which is not obtained from the optical measurement directly. In the near future we will study the surface integral in the case of linear optical constants, because such a study might give an answer to the question of, e.g., how to derive a sum rule, which is given using physical parameters, for the intensity reflectance of insulators or metals. This is an open question that has not been solved yet.[6,7] We also try to learn about the linear system to deal with the nonlinear case.

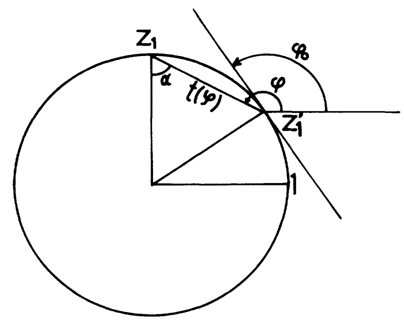

FIG. 1. The unit disk of integration of the surface integral. There is a pole z_1' on the boundary of the disk.

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APPENDIX

The result of Eq. (9) is well established in complex analysis. We briefly demonstrate the calculation of the surface integral in a simple case involving the term z_1 only. Using the notations indicated in Fig. 1 and a relation of $z_1-z_1'=r\exp(i\phi)$, we obtain the surface integral of the form

$$I=-\frac{c_1}{\pi}\int_{\phi_0}^{\phi_0+\pi}\int_0^{t(\phi)}\frac{r\,dr\,d\phi}{r\exp(i\phi)}\,, \tag{A1}$$

where $\phi_0=\arg z_1'+\pi/2$, $\alpha=-\pi+(\phi-\arg z_1')=\phi-\arg(-z_1')$. Taking into account, from Fig. 1, that $t=2\cos\alpha$, $-\pi/2\le\alpha\le\pi/2$, and substituting t, ϕ_0, and α into Eq. (11), we obtain the following result:

$$I=-\frac{2c_1}{\pi}\exp[-i\arg(-z_1)]\int_{-\pi/2}^{\pi/2}\exp(-i\alpha)\cos\alpha\,d\alpha$$
$$=c_1\bar{z}_1'\,. \tag{A2}$$

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[23]The Jacobian can be given, by using our notations $z=x+iy$ and $\hat{\omega}_1=\omega_1+iv$, as follows:

$$\frac{\partial(x,y)}{\partial(\omega_1,v)}=\begin{vmatrix}\dfrac{\partial x}{\partial\omega_1} & \dfrac{\partial x}{\partial v}\\ \dfrac{\partial y}{\partial\omega_1} & \dfrac{\partial y}{\partial v}\end{vmatrix}=\left[\frac{\partial x}{\partial\omega_1}\right]^2+\left[\frac{\partial y}{\partial\omega_1}\right]^2 .$$

This was obtained from the Cauchy-Riemann equations [for details, see, e.g., P. Henrici, *Applied and Computational Complex Analysis* (Wiley, New York, 1974), Vol. I].